06.1
.5
22p

67—2

Proceedings of the American Academy of Arts and Sciences.

Vol. 67. No. 2.—January, 1932.

PHYSICAL PROPERTIES OF SINGLE CRYSTAL MAGNESIUM.

By P. W. Bridgman.

Investigations on Light and Heat made and published with aid from the Rumford Fund.

(Continued from page 3 of cover.)

VOLUME 67.

1. BRIDGMAN, P. W.—Volume-Temperature-Pressure Relations for Several Non-Volatile Liquids pp. 1–27. January, 1932. $0.60.
2. BRIDGMAN, P W.—Physical Properties of Single Crystal Magnesium. pp. 29–41. January, 1932. $0.40.

Proceedings of the American Academy of Arts and Sciences.

Vol. 67. No. 2.—January, 1932.

PHYSICAL PROPERTIES OF SINGLE CRYSTAL MAGNESIUM.

By P. W. Bridgman.

Investigations on Light and Heat made and published with aid from the Rumford Fund.

PHYSICAL PROPERTIES OF SINGLE CRYSTAL MAGNESIUM.

By P. W. Bridgman.

Presented Oct. 14, 1931. Received Oct. 16, 1931.

Introduction.

The compressibility, specific electrical resistance, and pressure and temperature coefficients of resistance of single crystal magnesium in the crystallographically independent directions have already been reported in a previous paper.[1] To these are now added the five elastic constants, the thermo-electric properties, and the thermal expansion. Although the amount of this new material is not large, it has seemed better to give it in a small independent paper rather than to wait indefinitely until opportunity should present itself to publish it with related data for other materials.

The specimens whose thermo-electric properties and elastic constants are measured in this paper were the same as those whose electrical resistance was determined in the previous paper. The thermal expansion was measured on the two compressibility samples of the previous paper.

Detailed Data.

Thermo-Electric Properties. Measurements were made simultaneously on six crystal rods of different orientations in the same apparatus as previously used for thermo-electric measurements on a number of non-cubic crystals.[2] The ends of the rods were in contact with two different streams of rapidly circulating kerosene at different temperatures, and the thermo-electromotive force between the magnesium rods and copper leads was measured as a function of the variable temperature of the one stream, that of the other being maintained fixed at about 15.7° C. The upper temperatures were 37°, 56°, 75°, 96°, and a return check reading was made at 57°. Smooth curves of e.m.f. against temperature were then drawn through the observed points for each specimen, and the differences taken between the smooth curves and the straight lines joining the extreme points. The differences were then reproduced analytically by a three constant expression in the temperature of the form $at' + bt'^2 + ct'^3$, where the temperature of the cold junction is taken as 15.7°, and t' is the excess of the temperature of the hot junction above this. A three constant expression was adequate to reproduce the results within experimental error, but

a two constant expression was very distinctly not adequate. For most of the previous metals two constant expressions had been adequate. The calculation of the constants a, b, and c was facilitated by the fact that the maximum departure from linearity of the smooth curves for all orientations occurred at the same temperature, 35°. The constants a, b, and c were then plotted separately against $\cos^2\theta$, where θ is the angle between the principal axis of the crystal and the length of the specimen. If the Kelvin-Voigt symmetry relations hold, these three constants should each be linear in $\cos^2\theta$. The experimental evidence indicates that the Kelvin-Voigt relation is only an approximate relation, and that in Bi and Sn there are deviations beyond experimental error, although in Zn, Cd, and Sb the relation does seem to be satisfied within experimental error.[2] It would therefore have been most desirable to test the Kelvin-Voigt relation in magnesium also, but unfortunately the experimental accuracy was not great enough for this, and all that was possible was to assume the relation and to draw through the experimental points the best straight lines.

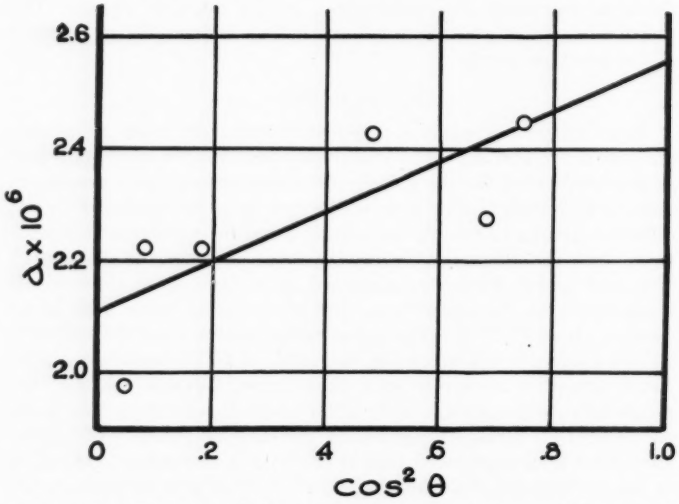

FIGURE 1. The constant "a" of the thermo-electric formula for rods of different orientations plotted as a function of the square of the cosine of the angle between the length of the rod and the crystal axis.

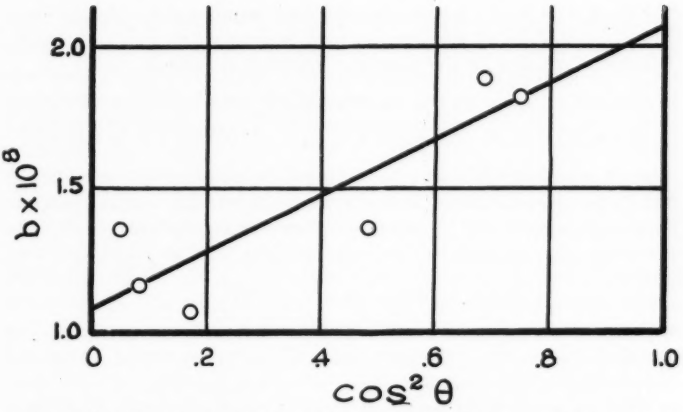

FIGURE 2. The constant "b" of the thermo-electric formula for rods of different orientations plotted as a function of the square of the cosine of the angle between the length of the rod and the crystal axis.

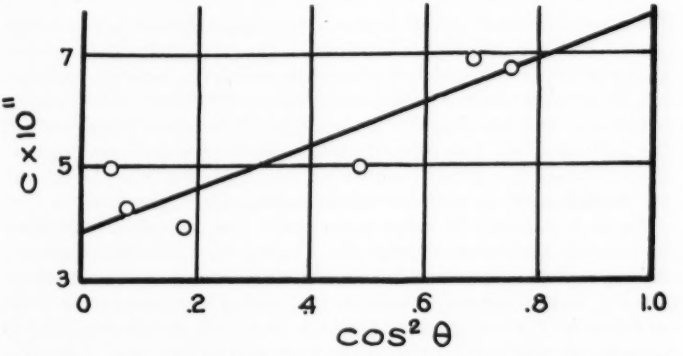

FIGURE 3. The constant "c" of the thermo-electric formula for rods of different orientations plotted as a function of the square of the cosine of the angle between the length of the rod and the crystal axis.

In figures 1, 2, and 3 the three constants a, b, and c are shown plotted against $\cos^2 \theta$, together with the straight lines taken to best represent the results. The intercepts of the lines at $\cos^2 \theta = 0$ and 1 give the

values of a, b, and c for the parallel and perpendicular orientations. Finally, the origin of temperature may be changed to 0° C, giving the following formulas for the thermo-electromotive force in volts:

$$(\text{t.e.m.f.})_{\perp-\text{Cu}} = 1.65 \times 10^{-6}t + 12.5 \times 10^{-9}t^2 - 3.8 \times 10^{-11}t^3,$$

$$(\text{t.e.m.f.})_{\parallel-\text{Cu}} = 1.85 \times 10^{-6}t + 24.3 \times 10^{-9}t^2 - 7.7 \times 10^{-11}t^3,$$

where t is ordinary Centigrade temperature. From these expressions the Peltier and Thomson heats between the parallel and the perpendicular directions may be found by differentiating once and twice.

$$P_{\parallel-\perp} = \tau[0.20 \times 10^{-6} + 23.6 \times 10^{-9}t - 11.7 \times 10^{-11}t^2],$$

$$\sigma_{\parallel-\perp} = \tau[23.6 \times 10^{-9} - 23.4 \times 10^{-11}t],$$

τ is absolute temperature. The sign convention is the usual one. A positive $(\text{t.e.m.f.})_{\perp-\text{Cu}}$ means that positive current flows from the perpendicular orientation to copper at the hot junction.

The mean of these results differs very considerably from that previously found for the e.m.f. between extruded polycrystalline commercial magnesium and copper.[3] The former result was:

$$(\text{t.e.m.f.})_{\text{Mg}-\text{Cu}} = 2.872 \times 10^{-6}t + 4.79 \times 10^{-9}t^2.$$

The great difference is doubtless to be partly explained by the single crystal condition, but also no doubt in large part by the superior purity of the new material, the former material having been commercial magnesium with a mean temperature coefficient of resistance between 0° and 20° of 0.0039 against 0.00432 between 0° and 100° of the new material. The temperature ranges are not the same, so that the results are not strictly comparable, but there can be no doubt that the coefficient of the new material is significantly higher.

Elastic Constants. The elastic constants were determined by combining with the measurements already made of the linear compressibility parallel and perpendicular to the axis new measurements of the bending and twisting of seven rods, thus giving 16 measurements in all to determine five constants. Six of the seven new rods were the same as those on which the thermo-electric properties had been measured, except that after the thermo-electric measurements were completed the rods were machined to true cylinders, the rough castings being too irregular to permit accurate determinations of the elastic constants. The machining was done in a jeweller's lathe with great care, using a sharp tool and removing a chip of only 0.001 inch at a time. No perceptible distortion of the rods was produced by the machining opera-

tion, but one or two of the rods had been slightly bent in getting out of the molds, so that it was necessary to straighten them before the machining could be done. The seventh rod was the same in all respects, except orientation, as the other six; its basal plane was practically perpendicular to the length, which is the direction of greatest plasticity.

The pieces of apparatus for bending and twisting were the same as those already used and described in connection with the alkali halides,[4] so that no further description is necessary. The bending measurements were made with four different orientations of each rod with respect to the weight; no variation with orientation could be detected in any case. The rods in their finally machined form were about 2.5 mm. in diameter, and the clear length between supports in the bending measurements was 4.2 cm. The load was 42 gm; the magnification was such that the deflections were several centimeters, and readings could easily be made to 0.1 mm. The probable accuracy was 1 or 2 %, as shown by the agreement of results obtained on the same specimen at different times with different set-ups. Twisting measurements were made with two different weights and several repetitions. The accuracy was about the same as for the bending measurements. Especial attention was given to the question of remaining within the elastic limit; this was probably always accomplished in the bending measurements, but it is less certain that the condition was met in the twisting measurements, and in fact the seventh rod, with the basal plane perpendicular to the length, showed very perceptible creep under load and elastic recovery on removal of load, although in bending no such effect was apparent. The twisting measurements on this specimen were made with a maximum twisting moment of only 25 gm cm instead of the usual 50, and furthermore the load was allowed to act for only a few seconds before readings. Even with these precautions there were noticeable creep effects, and furthermore the strain was not proportional to the load, but increased more rapidly. In the calculations the results with the smallest load were taken as most probably accurate, but the internal evidence is that the effect of creep was not entirely eliminated.

The equations connecting the elastic constants with the distortions may be found in Voigt's book Lehrbuch der Kristallphysik. The linear compressibilities are:

Perpendicular to axis, $s_{11} + s_{12} + s_{13} = 0.98 \times 10^{-9}$,

Parallel to axis, $2s_{13} + s_{33} = 0.98 \times 10^{-9}$,

The numerical values on the right hand sides of the equations are obtained from the linear compressibility measurements already reported.

For the bending of a rod of circular section, loaded at the center with weight Γ, and of total length L between end supports, Voigt gives on pages 746 and 747

$$s'_{33} = \frac{12\pi a^4}{\Gamma L^3} u,$$

where u is the deflection of the mid point and a the radius. Expressed in terms of the fundamental constants and the angle between the length of the rod and the axis,

$$s'_{33} = s_{11} \sin^4\theta + (2s_{13} + s_{44}) \cos^2\theta \sin^2\theta + s_{33} \cos^4\theta.$$

For the twist of a similar rod the formulas are:

$$n = \frac{N}{\pi a^4} (s'_{44} + s'_{55}),$$

where n is the twist per unit length, N the twisting moment, and

$$\tfrac{1}{2}(s'_{44} + s'_{55}) = s_{44} + (s_{11} - s_{12} - \tfrac{1}{2}s_{44}) \sin^2\theta + 2(s_{11} + s_{33} - 2s_{13} - s_{44}) \cos^2\theta \sin^2\theta.$$

In making the computations, the results on linear compressibility were accepted as absolutely correct, this having been justified by previous experience and the fact that the cubic compressibility calculated from the linear compressibility agrees with that of other observers determined by essentially different methods. The effective constants s'_{33} and $s'_{44} + s'_{55}$, as given by the bending and twisting measurements, were now plotted against $\cos^2\theta$, and curves drawn through these points in such a way as to pass as close to the points as possible and at the same time give values for the fundamental constants which should be consistent with the linear compressibility measurements. In figures 4 and 5 are shown the observed values of s'_{33} and $s'_{44} + s'_{55}$ plotted against $\cos^2\theta$ and the curves drawn through them. The fundamental constants were calculated from the intercepts of the curves at the two extreme points and at the mid point, $\cos^2\theta = 0.50$. Thus, from the bending curve, the value of s'_{33} when $\cos^2\theta = 0$ is s_{11}, its value when $\cos^2\theta = 0.50$ is $\frac{1}{4}[s_{11} + s_{33} + (2s_{13} + s_{44})]$, and its value when $\cos^2\theta = 1$ is s_{33}. The values of the effective twisting modulus $(s'_{44} + s'_{55})$ for corresponding values of $\cos^2\theta$ are

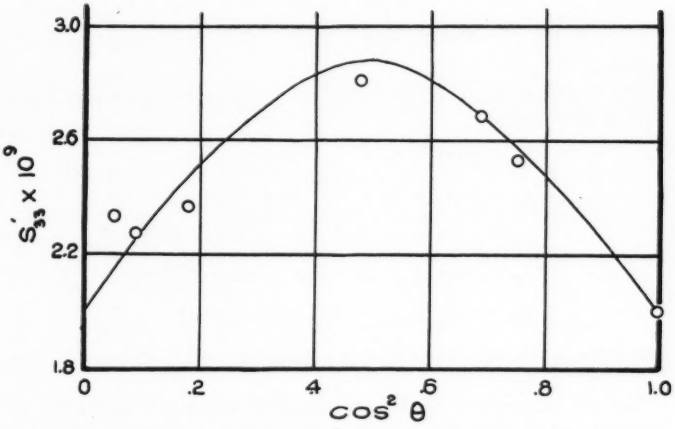

FIGURE 4. The effective elastic constant s'_{33} for rods of different orientations plotted as a function of the square of the cosine of the angle between the length of the rod and the crystal axis.

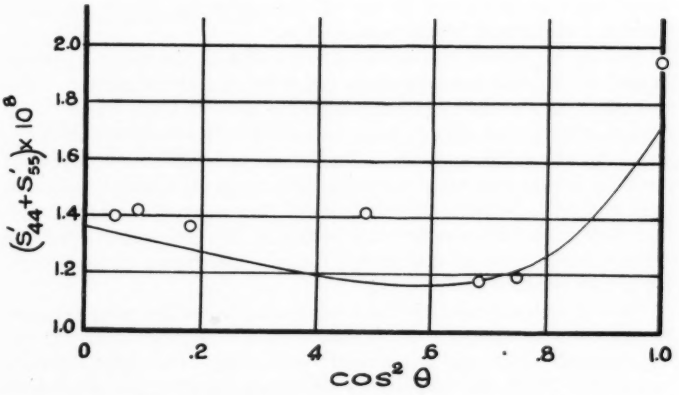

FIGURE 5. The effective elastic constant $s'_{44} + s'_{55}$ for rods of different orientations plotted as a function of the square of the cosine of the angle between the length of the rod and the crystal axis.

$$(2s_{11} - 2s_{12} + s_{44}), \quad \left(2s_{11} - s_{12} - 2s_{13} + s_{33} + \frac{s_{44}}{2}\right),$$

and $2s_{44}$.

The following are the values of the fundamental constants calculated in this way:

$$s_{11} = 2.00 \times 10^{-9} \quad \text{or} \quad 20.4 \times 10^{-13},$$

$$s_{33} = 2.00 \times 10^{-9} \quad \text{or} \quad 20.4 \times 10^{-13},$$

$$s_{13} = -0.51 \times 10^{-9} \quad \text{or} \quad -5.2 \times 10^{-13},$$

$$s_{12} = -0.51 \times 10^{-9} \quad \text{or} \quad -5.2 \times 10^{-13},$$

$$s_{44} = 8.62 \times 10^{-9} \quad \text{or} \quad 87.8 \times 10^{-13}.$$

The units in the first set of figures are gm cm and in the second Abs. C. G. S.

The self consistency of the experimental results, as shown by the closeness with which the curves pass through the experimental points, is in all cases satisfactory except for two points on the twisting curve. Both of these points are too high; the one corresponding to $\cos^2\theta = 1$ (basal plane perpendicular to the length) is doubtless in error because of the extreme softness of the specimen, as already explained, and the other point at $\cos^2\theta = 0.50$ lies off the curve by about the same amount and perhaps for the same reason.

Thermal Expansion. This was determined with the same apparatus as used in previous measurements, but it was freshly calibrated. The specimens, as already mentioned, were the same as those whose linear compressibility had already been measured. The temperature range was from about 35° to 15° C. The former procedure was somewhat modified in that instead of repeating measurements a number of times back and forth between the extremes of the temperature range, readings were made with smaller steps both with decreasing and increasing temperature, covering the entire range. Somewhat greater regularity was attained in this way.

There is an uncertainty in the final results due to the value assumed for the thermal expansion of the mild steel of which the apparatus was constructed, which was not directly measured. The value assumed was 12.0×10^{-6}; this value enters additively into the final result with a factor $\frac{1}{5}$, and affects measurements on both orientations equally, so that the resultant uncertainty is too small to be significant.

The results found for the linear expansion are:

Parallel to the axis, 27.1×10^{-6}.

Perpendicular to the axis, 24.3×10^{-6}.

This gives for the mean expansion of a polycrystalline aggregate 25.2×10^{-6}. International Critical Tables gives for ordinary polycrystalline magnesium 25.6×10^{-6}.

Discussion.

For convenience the constants determined in the previous paper are reproduced here.

Linear Compressibility.

Parallel to the axis:

$$\text{At } 30°, \quad -\Delta l/l_0 = 9.84 \times 10^{-7}p - 6.51 \times 10^{-12}p^2.$$

$$\text{At } 75°, \quad -\Delta l/l_0 = 10.15 \times 10^{-7}p - 7.78 \times 10^{-12}p^2.$$

Perpendicular to the axis:

$$\text{At } 30°, \quad -\Delta l/l_0 = 9.84 \times 10^{-7}p - 9.19 \times 10^{-12}p^2.$$

$$\text{At } 75°, \quad -\Delta l/l_0 = 9.66 \times 10^{-7}p - 6.95 \times 10^{-12}p^2.$$

p is in kg/cm^2.

Electrical Resistance.

Specific resistance:

Parallel to the axis, 3.89×10^{-6}
Perpendicular to the axis, 4.60×10^{-6} } at 22°.5 C.

Effect of pressure on resistance:

Axis 73° to length:

$$\text{At } 30°, \quad -\frac{\Delta R}{R(0, 30°)} = 5.61 \times 10^{-6}p - 8.4 \times 10^{-11}p^2.$$

$$\text{At } 75°, \quad -\frac{\Delta R}{R(0, 75°)} = 5.67 \times 10^{-6}p - 8.35 \times 10^{-11}p^2.$$

Axis 29° to length.

$$\text{At } 30°, \quad -\frac{\Delta R}{R(0, 30°)} = 5.48 \times 10^{-6}p - 7.8 \times 10^{-11}p^2.$$

$$\text{At } 75°, \quad -\frac{\Delta R}{R(0, 75°)} = 5.99 \times 10^{-6}p - 11.8 \times 10^{-11}p^2.$$

Temperature coefficient of resistance.

Axis 73° to length, mean coefficient 0°–100° = 0.00439.

Axis 29° to length, mean coefficient 0°–100° = 0.00420.

A paragraph is also quoted from the discussion in the previous paper:

"Magnesium is of interest because it is the first hexagonal metal measured in which the axial ratio corresponds to a packing of *spheres* in close packed hexagonal array. The piling in Zn and Cd, for example, is that of close packed ellipsoids. It is, of course, well known that the close packed hexagonal arrangement of spheres differs little from the close packed face centered cubic arrangement. In fact, if the two arrangements are built up by piling over each other layers perpendicular to the hexagonal axis, the only difference between the two arrangements is a slight relative displacement of the third layers, the first and second layers in the two arrangements being the same. Hence the forces on the atoms in the two arrangements can differ only by the contributions of the more distant atoms, which are unimportant because of the rapid falling off of atomic forces with increasing distance. It follows that a close packed hexagonal arrangement of spheres would not be expected to differ greatly in physical properties from a close packed cubical arrangement, and in particular, the compressibility of the hexagonal arrangement would be expected to be nearly the same parallel and perpendicular to the axis, because the compressibility of a cubic crystal is the same in all directions."

The expectation that magnesium would be like a cubic crystal in many respects is fulfilled in the first place by the linear compressibilities, which are the same in different directions within experimental error. Most of the elastic constants show the same sort of thing. Consider the "square" constants s_{11}, s_{33}, s_{12}, and s_{13}, called "square" because no shearing strains or stresses are involved, but these constants connect the elongations parallel and perpendicular to the axis with the normal stresses across the corresponding planes. For a cubic crystal these four square constants reduce to two, s_{11}, s_{11}, s_{12}, and s_{12} respectively. We notice at once that the four constants for hexagonal magnesium reduce in exactly the same way to two, that is, $s_{11} = s_{33}$, and $s_{13} = s_{12}$. s_{11} and s_{33} measure the effective Young's modulus for rods cut perpendicular and parallel to the crystal axis, so that we see that the extensibility under a one sided extending stress is the same for directions parallel and perpendicular to the axis, just like the linear

compressibility. In the same way s_{12} and s_{13} measure the effective Poisson's ratio for rods parallel and perpendicular to the axis, and these again are equal. As far as this type of deformation is concerned, therefore, magnesium behaves much like a cubic substance.

The shearing constant, however, does not follow the type of the cubic crystal. In a cubic crystal the three principal shearing constants s_{44}, s_{55} and s_{66} are all equal. In a hexagonal crystal like magnesium, on the other hand, s_{44} and s_{55} are equal to each other, but s_{66} is different and identically equal to $2(s_{11} - s_{12})$. Hence if the shearing constants of magnesium were like those of a cubic crystal we would have for it $s_{44} = 2(s_{11} - s_{12})$. As a matter of fact, the numerical values are 87.8 and 51.2×10^{-13} respectively, so that the cubic relation fails by an amount far beyond possible experimental error.

The failure of the cubic relation for the shearing constants reacts on the effective Young's modulus of rods inclined to the axis, and it will be found that the Young's modulus of rods neither parallel nor perpendicular to the axis is not quite the same as for these two directions, so that with regard to the complete reaction to tension, magnesium does not behave like a cubic crystal, although it does with respect to hydrostatic pressure.

In view of the complete elastic symmetry with respect to hydrostatic pressure, it was a surprise to find the distinct failure of isotropy with respect to thermal expansion, which in the direction perpendicular to the axis is only 0.90 of the value parallel to the axis. This difference is consistent with the behavior of other metallic crystals, the thermal expansion usually being greatest across the basal plane, that is, the plane of easiest slip. For example, in Zn and Cd the ratio of the expansions perpendicular to parallel are 0.22 and 0.39 respectively. In the case of Zn and Cd, however, the ratio of the expansions is nearer to unity than the ratio of the compressibilities, whereas in Mg the reverse is the case. The behavior of the thermal expansion is somewhat in line with other temperature parameters, for it has already been found that the temperature coefficient of compressibility is markedly different in different directions, as is also the temperature coefficient of resistance. It is evident, therefore, that different effects are influenced in different degrees by the similarity of the structure of magnesium to the cubic structure.

With regard to thermo-electric properties, magnesium is like all the other non-cubic metals studied exeept tin, in that the Peltier heat at 0° between the parallel and perpendicular directions of flow is positive,

but the effect is unusually small in magnesium, being only 0.55×10^{-4} against 4.90×10^{-4} for zinc, for example. In a cubic crystal the Peltier heat between any two directions is of course zero, so that with regard to Peltier heat magnesium again approaches a cubic crystal. The Thomson heat, however, is different, because $\sigma_{\parallel-\perp}$ for magnesium has the value 6.43×10^{-6}, and this is somewhat larger than for any of the other non-cubic metals except bismuth, where large effects are always to be expected. The sign of $\sigma_{\parallel-\perp}$ is the same for magnesium as for all the other non-cubic metals except bismuth. This confirms a conclusion previously reached on other grounds that there is not much similarity between the Peltier and Thomson heat mechanisms.

The manuscript of this paper was ready for publication when a preliminary notice, without experimental details, was published by Goens and Schmid[5] giving the specific resistance, temperature coefficient of resistance, and elastic constants of single crystal magnesium. The results of our two measurements are not as consistent as they ought to be. The greatest discrepancies are in the elastic constants. The values of Goens and Schmid are:

$$s_{11} = 22.3 \times 10^{-13}, \quad s_{33} = 19.8 \times 10^{-13}, \quad s_{44} = 59.5 \times 10^{-13},$$
$$s_{12} = -\ 7.7 \times 10^{-13}, \quad s_{13} = -\ 4.5 \times 10^{-13}.$$

The method of Goens and Schmid was a dynamic method in distinction from the static method used here. The greatest difference in our constants is in s_{44}. The values of Goens and Schmid of the constants would demand that the curve of figure 4 have the ordinate 22.7 at $\cos^2\theta = 0.5$, and in figure 5 the ordinate at $\cos^2\theta = 1$ would have to be 1.17; neither of these values seem possible for my material and my method.

The specific resistance of Goens and Schmid, parallel to the axis, reduced to 22.5°, is 3.84×10^{-6} against my 3.89×10^{-6}, and perpendicular to the axis they had 4.63 against my 4.60. The value to be calculated for polycrystalline material from these figures is almost identically the same for both of us. Their mean temperature coefficients of resistance parallel and perpendicular are 0.00427 and 0.00416 against my 0.00413 and 0.00441 respectively, a reversal of order to which they have already called attention, and which is not easy to account for.

Their thermal expansions parallel and perpendicular, making a linear correction for the difference of temperature range, are 25.5 ×

10^{-6} and 24.9×10^{-6} respectively, against my 27.1 and 24.3. The calculated values for volume expansions are 75.3 and 75.7 respectively.

The discrepancies are not easy to account for. The first thing to suspect is difference of purity. They do not give in their preliminary communication the method of casting the crystal or the sort of mold used, but state that the purity of the initial material was 99.95%. The values given above for the specific resistance would indicate no difference in the purity of our respective material, while the temperature coefficients would indicate a slight superiority of mine. The discrepancy in the elastic constants may be due to the difference of methods. It is to be noticed that their value for the shearing constant s_{44} is much more like that of a cubic metal than mine; it is important for theoretical reasons that the discrepancy be explained.

I am indebted to my assistant Mr. L. H. Abbot for the measurements of thermal expansion. I am also indebted for financial assistance to the Milton Fund of Harvard University and the Rumford Fund of the American Academy of Arts and Sciences.

The Jefferson Physical Laboratory,
Harvard University, Cambridge, Mass.

References.

[1] P. W. Bridgman, Proc. Amer. Acad. 66, 255–271, 1931.
[2] P. W. Bridgman, Proc. Amer. Acad. 63, 351–399, 1929.
[3] P. W. Bridgman, Proc. Amer. Acad. 53, 305, 1918.
[4] P. W. Bridgman, Proc. Amer. Acad. 64, 19–38, 1929.
[5] E. Goens and E. Schmid, Die Naturwiss, 18, 376–377, 1931.